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54. Name of Invention

Electrodeposition Painting Method

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72. Inventor
Eisaku Nakatani

72. Inventor
Masayuki Misawa

72. Inventor
Teiji Katayama

72. Inventor
Mitsuyoshi Kitano

71. Applicant
Kansai Paint CO., Ltd.

Specification
1. Name of Invention

Electrodeposition Painting Method

2. Claim

1. The electrodeposition painting method characterized by having a paint consisting mainly of an epoxy based cationic electrodeposition resin (a) which has its surface tension of 40-60 dyne/cm and can form an aqua basic bath capable of being electrodeposited on a cathode when neutralized with acid and of at least one granular compound which is chosen from gelled polymer fine particulate or pigment, and mainly consisting of a cationic electrodeposition resin (c) which can form an aqua basic bath capable of being electrodeposited on a cathode by neutralizing a cationic electrodeposition paint composite (A) which has its surface tension of 40-60 dyne/cm when the coating film obtained from the above-mentioned paint is cured with acid on an electrodeposition coating film on a un-cured electrodeposition coating film which is obtained by electrodepositing on a material to be coated, with its surface tension of 25-45 dyne/cm, and by being able to bake and cure a un-cured electrodeposition coating film which is formed by electrodepositing cationic electrodeposition paint component (B) having a smaller surface tension than that of a cationic electrodeposition resin (a).
2. The electrodeposition painting method of Claim 1 characterized by having an addition reaction product of an epoxy resin and a basic amino compound as the epoxy based cationic electrodeposition resin (a) which is a main component of the cationic electrodeposition painting composite (A).
3. The electrodeposition painting method of Claim 1 characterized by having an addition reaction product of at least one of epoxy resin, acrylic resin and polyester resin, and of the basic amino compound as cationic electrodeposition resin (c) which is a main component of the cationic electrodeposition painting composite (B).
4. The electrodeposition painting method of Claim 1 characterized by having an internally cross-linked gelled polymer with alkoxysilane group and cationic group as the gelled polymer fine-particle used for the cationic electrodeposition painting composite (A).
5. The electrodeposition painting method of Claim 1 characterized by having silicon dioxide system paints with 100 or more of oil absorption capacity and carbon system paints as the pigment used for the cationic electrodeposition painting composite (A).

3. Detailed Explanation of Invention

(Field of the Invention)

This invention is about the cationic electrodeposition painting method, and especially the method in which it is possible to cover edges of the angle part of a cut surface, the bend part, and the projection part with thick films, and is excellent in coated surface smoothness and coated surface smoothness by

(Prior Art and its Problems)

The cationic electrodeposition paint is excellent in its throwing power of electrolytic coloring and in its film thickness evenness, and the coating film obtained from it is excellent in surface

smoothness, and therefore, it has been used for prime coating of car body, etc.

However, even though the cationic electrodeposition paint is excellent in its surface smoothness since it usually has low melt viscosity at the time of being cured, the cured coating film is not formed on edge parts, and therefore, it tends to cause the rust resistance characteristic of the edge parts to fall.

Although rust resistance steel plates are used or the repair paint of the corrosive protection paint using the roller, brush, etc. is carried out on the edge parts following the electrodeposition and the baking in order to improve the rust resistance characteristic of the edge parts, this is very costly and requires a large number of processes.

Moreover, although mixing of pigment into the electrodeposition paint in large amount or decreasing the amount of plastic components are both carried out, it has been still difficult to obtain both the edge cover and the surface smoothness at the same time.

Although the electrodeposition paint is carried out twice, it has not yet come to satisfy the above-mentioned both characteristics.

There has been a demand for development of the cationic electrodeposition painting method with which it is possible to obtain the above-mentioned both characteristics

(Means to Solve the Problem)

As a result of carrying out many research in order to obtain a cationic electrodeposition painting method which can give both excellent edge cover and surface smoothness, the inventors of this invention has come to realize that it is possible to obtain a multiple layered electrodeposition coating film which has both excellent edge cover and surface smoothness, by creating the first layer of the electrodeposition painting with the cationic electrodeposition painting composite whose melt viscosity decrease at the time of baking and curing is controlled by blending an epoxy based cationic electrodeposition resin which has its surface tension in a specific range and at least one granular compound which is chose from gelled polymer fine particulate or pigment, and by creating the second layer of the electrodeposition painting with the cationic electrodeposition painting composite which has its surface tension in a specific range and uses a cationic electrodeposition resin which has smaller surface tension than that of the cationic electrodeposition resin of the first layer.

That is, this invention is about the electrodeposition painting method characterized by having a pain consisting mainly of an epoxy based cationic electrodeposition resin (a) which has its surface tension of 40-60 dyne/cm and can form an aqua basic bath capable of being electrodeposited on a cathode when neutralized with acid and of at least one granular compound which is chose from gelled polymer fine particulate or pigment, and mainly consisting of a cationic electrodeposition resin (c) which can forming an aqua basic bath capable of being electrodeposited on a cathode by neutralizing a cationic electrodeposition paint composite (A) which has its surface tension of 40-60 dne/cm when the coating film obtained from the above-mentioned paint is cured with acid on a electrodeposition coating film on a un-cured electrodeposition coating film which is obtained by

electrodepositing on a material to be coated, with its surface tension of 25-45 dyne/cm, and by being able to bake and cure a un-cured electrodeposition coating film which is formed by electrodepositing cationic electrodeposition paint component (B) having a smaller surface tension than that of a cationic electrodeposition resin (a).

According to this invention, when carrying out the baking and the curing of the electrodeposition coating films of the first and the second layers at the same time, the two layers can be moderately separated since the two is not mixed due to the differences in the surface tensions, and therefore, it is possible to attain the edge cover characteristic which prevent rust from generated with the first layer and to attain the surface smoothness and the weather-proof characteristic with the second layer.

In this invention, the cationic electrodeposition paint composite (A) is used for the first layer of the electrodeposition paint which forms the electrodeposition multiple layer coating film, and contains the epoxy based cationic electrodeposition resin (a) whose surface tension is within the range of 45-55 dyne/cm, or suitably 40-60 dyne/cm.

As for the epoxy based cationic electrodeposition resin (a), polyamine resin such as amine addition epoxy resin which has been used in the cationic electrodeposition paint field, for example, (I) addition product of polyepoxide and primary mono and polyamine, secondary polyamine, or primary and secondary mixture polyamine (for example U.S. patent NO. 3,984,299); (II) addition product of polyepoxide compound and secondary mono and polyamine which has ketimine primary amine group (for example, U.S. patent NO. 4,017,438); and (III) addition reaction product obtained by etherealization of polyepoxide compound and hydroxy compound which has ketimine primary amine group (for example, Japan Unexamined Patent Publication Showa 59-43013), can be used.

As for the polyepoxide compound used to manufacture the above-mentioned polyamine resin, it is desirable to use the compound which has at least two of the epoxy group (inset figure) in one molecule, and has at least 200 of the number average molecular weight, preferably in the range of 400-4000, or more preferably in the range of 800-2000, and the compound which is obtained by the reaction of polyphenol compound and epoxypropyl diethylenetriamino.

As for the polyphenol compound used to form this polyepoxide compound, for example, bis (4-hydroxyphenyl)-2,2-propane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bis(4-hydroxyphenyl)-1,1-isobutane, bis(4-hydroxy-tert-butyl-phenyl)-2,2-propane, bis(2-hydroxynaphthyl) methane, 1,5-dihydroxynaphthalene, bis(2,4-dihydroxyphenyl) methane, tetra (4-hydroxyphenyl)-1,1,2,2-ethane, 4,4-dihydroxy diphenyl sulfone, phenol novolak, cresol novolak etc., are mentioned.

This polyepoxide compound can be partially reacted with polyol, polyether polyol, polyester polyol, polyamide amine, polycarboxylic acid, poly isocyanate compound etc., furthermore, a graft polymerization of acrylics monomer etc., can also be carried out to this.

The above-mentioned amine addition epoxy resin can be cured with polyisocyanate compound which is blocked with alcohol, etc., or with cross-linking agents, such as melamine resin, if needed.

Moreover, the amine addition epoxy resin capable being cured without using the above-mentioned cross-linking agents can also be used, and for example, resin in which β -hydroxyalkylcarbamate group is introduced to a polyepoxide substance (for example, Japan Unexamined Patent Showa 59-155470); resin which can be cured by an ester exchange reaction (for example, Japan Unexamined Patent Publication Showa 55-80436); or resin in which block isocyanate group is introduced to the basic resin can also be used.

It is necessary for the epoxy based cationic electrodeposition resin (a) used in this invention to have its surface tension of 40-60 dyne/cm as listed above, or preferably to be in the range of 45-55 dyne/cm.

When the surface tension is lower than 40 dyne/cm, it becomes difficult to form layer coating film since the first layer tends to be mixed with the second layer which becomes the graze, and the rust prevention characteristic of the first layer which becomes the prime and the weather proof characteristic of the second layer will be inferior.

On the other hand, when the surface tension exceeds 60 dyne/cm, the adhesion between the layers of the first layer coating film and the second layer coating film will be inferior, and therefore, it is not desirable.

In this invention, "surface tension" is measured as follows:

Resin (a) or resin (c) which is diluted with solvent is painted on the smooth tin board which is degreased using a bar-coater so that the dried coating film becomes 10 μ m.

The coating film is air dried at the room temperature for 1 day, and after it is dried with the 50DEGC/0.1 atmospheric pressure for 1 hour, the measurement listed below is carried out at the room temperature after 10 minutes passed.

The contact angle (θ) to the above-mentioned dried resin is measured by dropping deionization water.

Subsequently, the surface tensions of resin (a) or resin (c) are measured according to the empirical formula of Sell and Neumann. γ

$$\cos \theta = \frac{(0.015 \gamma_a - 2) \sqrt{\gamma_a \gamma_L} + \gamma_L}{\gamma_L (0.015 \sqrt{\gamma_a \gamma_L} - 1)}$$

The inside of a formula: γ_L : Surface tension of water (72.8 dyne/cm)
 γ_a : Surface tension of resin (a) or resin (c) (dyne/cm)

In this invention, the granular component (b) which is the other main component of the cationic electrodeposition paint composite (A) is used to control the decrease in the melt viscosity at the time of being cured, and is chosen from at least one type of gelled polymer fine-particle and pigments.

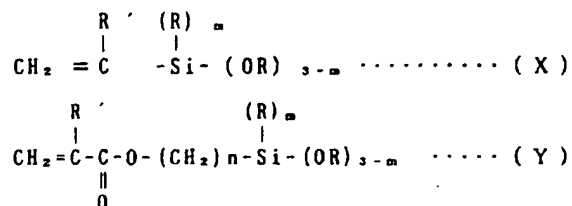
As for the gelled polymer fine-particle used for the cationic electrodeposition paint composite (A) in this invention, the product which is obtained by carrying out a aqueous dispersion of acrylics system copolymer containing hydrolysis nature alkoxy silane group and cationic group and by carrying out an internal cross-linking, can be used.

This acrylics system copolymer is dispersed stably in water with cationic group and especially with amino group which is neutralized with acid as water dispersive, and forms a gelled polymer fine-particle capable of being electrodeposited with cation by being gelled from internal cross-linking generated by the condensation of silanol group generated by the hydrolysis of alkoxy silane group with other silanol or with hydroxyl group when hydroxyl group exists in the acrylics system copolymer.

Generally, this acrylics system copolymer is manufactured by carrying out a copolymerization of a monomer mixture which consists of

- (I) polymerization unsaturated vinylsilane monomer containing vinyl nature double bond and a hydrolysis nature alkoxy silane group, and
- (II) polymerization unsaturated monomer containing a vinyl nature double bond and a cationic group, as required components for the monomer, and
- (III) polymerization unsaturated monomer containing a vinyl nature double bond and a hydroxyl group-and/or
- (IV) and other polymerization unsaturated monomer, if necessary.

The above-mentioned vinyl silane monomer (I) has the product represented by the following general formula.



[In the formula,

R¹ expresses an alkyl group or an alkoxyalkyl group with 1-10 carbon atom,

R² expresses a hydrogen atom or a methyl group,

m expresses an integer of 0 or 1,

n expresses the integer of 1-8.]

As for the vinyl silane monomer shown by the above-mentioned (X) formula, for example,

vinyl trimethoxysilane,

vinyl triethoxysilane, and

vinyl tris-(3-methoxy ethoxysilane) etc., can be mentioned,

and, as for the vinyl silane monomer shown by the above-mentioned (Y) formula, for example,

γ -acrylics oxypropyl trimethoxysilane,

γ -methacryloxy propyl trimethoxysilane, and

γ -methacryloxy propylmethyl dimethoxysilane, etc., can be mentioned,

and above all, γ -methacryloxy propyl trimethoxysilane is most suitable.

The polymerization unsaturated monomer represented with the above (II) containing the vinyl nature double bond and cationic group is a monomer component which introduces the cationic group which gives a water dispersibility to the generated acrylics system copolymer.

As for the cationic group,

tertiary amino group,

quaternary ammonium base,

tertiary sulfonium base,

quaternary phosphonium base etc., can be used, and among those, tertiary amino group is especially desirable.

As for the monomer containing a vinyl nature double bond and a tertiary amino group, for example,

dialkyl aminoalkyl (meta) acrylate, such as

dimethylamino propyl (meta) acrylate,

and diethylamino ethyl (meta) acrylate,

(these alkyl are preferably the alkyl with 1-6 carbon atom);

or dialkyl aminoalkyl (meta) acrylics amide, such as

dimethylamino propyl (meta) acrylics amide,

and diethylamino ethyl (meta) acrylics amide etc.

(these alkyl are preferably the alkyl with 1-6 carbon atom)

can be mentioned.

As for the polymerization unsaturated monomer containing a quaternary ammonium base and a vinyl nature double bond, for example,

3-acrylamide-3-methylbutyl trimethyl ammonium chloride,

3-methacryl amide-propyl trimethyl ammonium chloride, and

2-methacryloyloxy ethyl trimethyl ammonium chloride etc., are mentioned.

The polymerization unsaturated monomer represented with the above (III) containing vinyl nature

double bond and hydroxylic base is a monomer component which introduces a hydroxyl group into an acrylics copolymer if needed, and the hydroxyl group works as a functional group at the time of aqueous dispersion of acrylics system copolymer and/or as a hydrophilic group for the cross-linking reaction inside of a distributed particle.

As for this unsaturated monomer, for example, hydroxy alkyl ester of (meta) acrylic acid, such as 2-hydroxy ethyl (meta) acrylate, and hydroxy propyl (meta) acrylate etc., are mentioned.

The other polymerization unsaturated monomer represented with the above (IV), is the remaining components which constitutes the acrylics system copolymer, and for example, the well-known monomer used for composition of the usual acrylic resin, such as alkyl (C1-C18) ester of which (meta) acrylic acid, such as methyl (meta) acrylate, ethyl (meta) acrylate, propyl (meta) acrylate, isopropyl (meta) acrylate, buthyl (meta) acrylate, hexyl (meta) acrylate, octyl (meta) acrylate, lauryl (meta) acrylate, and cyclohexyl acrylate; vinyl aliphatic monomer; such as styrene, α -methyl styrene, and vinyltoluene; amide derivative of (meta) acrylic acid which does not contain tertiary amino group; or (meta) Acrylonitrile; can be used.

These monomer (IV) can be suitably chosen according to the characteristic required for the generated acrylics system copolymer, and may be used independently or may be used by being combed with two or more types.

It is suitable for the above-mentioned monomers (I)-(IV) which constitute the acrylics system copolymer in this invention to be used in the range of the combination rate described below.

- (I) monomer: 1-30 % weight%, or desirably 3-20 % weight%
- (II) monomer: 5-30 % weight%, or desirably 5-25 % weight%
- (III) monomer: 0-30% weight%, or desirably 5-20 % weight%
- (IV) monomer: 10-94 % weight%, or desirably 35-82 % weight%

As for another method of manufacturing the acrylics system copolymer containing a hydrolysis nature alkoxysilane group and a cationic group, the method in which after copolymerization of the above-mentioned (I)-(IV) monomers are carried out by using a glycidyl group content unsaturated vinyl monomer (for example, glycidyl acrylate, glycidyl metacrylate etc.) instead of using the

above (II) and a acrylics system copolymer containing a glycidyl group, a tertiary amine group or a quaternary ammonium base is introduced to the glycidyl group by making a secondary amine or a tertiary amine group to react or a tertiary sulfonium base or a quaternary phosphonium base is introduced by making a secondary sulfide salt or a tertiary phosphine salt, can be mentioned.

Usually, it is desirable to introduce the tertiary amino group.

A well-known method used for manufacturing acrylics system copolymers or the solution polymerization method can be applied for the copolymerization of the unsaturated monomers of above-mentioned (I)-(IV).

For example, it can be done by carrying out a reaction of the above-mentioned monomer mixture in a suitable solvent in the presence of a radical polymerization catalyst with the reaction temperature of about 0-180DEGC for about 1-20 hours

As for the solvent used for this invention, the solvent which can dissolve the generated copolymer and can also be mixed with water in order to prevent a gelation while the copolymerization is in the progress.

As for this solvent, for example,
alcoholic system solvent,
ether alcoholic system solvent,
ether system solvent,
ketone system solvent,
and ster system solvent etc. can be used.

Moreover, as for the polymerization catalyst, for example,
azo system compound,
peroxide system compound,
sulfide,
sulfin
diazo compound,
and nitroso compound etc. can be used.

Moreover, in order to prevent the polymer to generate particles or to remove moisture that works as a catalyst of a cross-linking reaction caused by the cross-linking reaction of alkoxysilane in the middle of a copolymerization reaction, it is possible to carry out a polymerization by adding dehydrators, such as a dimethoxy propane.

Generally, the acrylics system copolymer obtained in this way has
its amine value of 10-about 100, or more preferably about 15-80;
its hydroxylic base value of 0-about 200, or more preferably about 30-130;
and its number average molecular weight of about 5.000-about 100.000, or more preferably about 7.000-30.000.

When the amine value of the acrylics system copolymer is smaller than 10, dispersibility in the

water becomes insufficient, and generally it becomes easy to form a big and rough particle.

On the other hand, when the amine value is larger than 100, it becomes easy to cause gelling at the time of the solution polymerization.

Moreover, when the number average molecular weight of the acrylics system is smaller than 5,000, the dispersibility often becomes poor or the degree of gelling falls.

On the other hand, when the number average molecular weight is larger than 100,000, the viscosity tends to become too large and it becomes difficult to carry out the aqueous dispersion.

The aqueous dispersion of the above-mentioned acrylics system copolymer can be carried out by following the well-known method.

For example, it can be carried out by neutralizing the alkoxysilane group and the cationic group or the acrylics system copolymer containing a hydroxyl group obtained by the process listed above, with about 0.1-1 Eq of acid like water-soluble carboxylic acid, such as formic acid, acetic acid, lactic acid, or hydroxyl acetic acid, to the amino group when the cationic group is an amino group, and by dispersing it with water so that the solid part concentration may become about 40 or less weight%.

The distributed particle of the aqueous dispersion product of the acrylics system copolymer obtained in this way is cross-linked internally.

Although the cross-linking is possible to some extent by only storing this dispersion product for a long period of time, it is desirable to advance the cross-linking reaction by heating this aqueous dispersion to the temperature of about 50 or more DEG C.

Or, when carrying out the aqueous dispersion of the above-mentioned acrylics system copolymer, it is possible to carry out the aqueous dispersion and the internal cross-linking at the same time by adding silanol group concentrated catalyst such as octyl sulfonate, octyl zinc, octyl zirconium, and dibutyl laurate can be added in copolymer solution or a water medium, and by carrying out the aqueous dispersion in the presence of these catalyst.

Thus, the gelled polymer particulate aqueous dispersion solution manufactured in this way usually has about 10-40% weight% of the resin solid content.

Generally, the particle diameter of a distributed particle is within the limits of 0.5 or less μm , preferably of 0.01-0.3 μm , or more preferably of 0.05-0.2 μm .

It is possible to adjust the particle diameter by adjusting the amount of the cationic group in the acrylics system copolymer, and the desired range can be easily attained.

As for the gelled polymer fine-particle used in this invention, particles to which aqueous dispersion is carried out by mixing cationic acidity colloidal silica to the above-mentioned acrylics copolymer can be used.

As for this cationic acidity colloidal silica, it is desirable to use the colloidal silica, whose surface is cationic, whose dispersion solution is acidic, which is an aqueous dispersion with SiO_2 as its unit, and whose diameter of an average particle is in the range of 0.004-0.1 μm .

Although the mixture ratio of the above-mentioned acrylics system copolymer and cationic acidity colloidal silica is not especially limited, it is desirable to have the cationic acidity colloidal silica in 1-50 weight part, or preferably in 5-20 weight part to 100 weight part of the acrylics system copolymer.

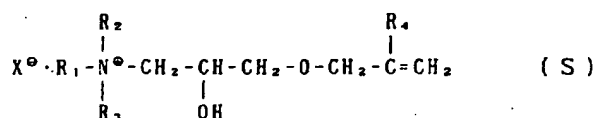
As for the gelled polymer fine-particle used in this invention, the particle which is formed by using polymerization monomer which contains at least 2 of the unsaturated group and in which a radical polymerization is possible in a molecule for the unsaturated monomers (I)-(IV) used for the manufacture of the above-mentioned acrylics copolymer instead of the monomer (II), and by carrying out an emulsification polymerization of this unsaturated monomers with cationic nature reactivity emulsifier containing an allyl group, can be mentioned.

As for the above-mentioned "the polymerization monomer which contains at least 2 of the unsaturated group and in which a radical polymerization is possible in a molecule", there are polymerization unsaturated mono carboxylic ester of multi-value alcohol, polymerization unsaturated alcohol ester of multi-base acid, or aromatic compounds which is replaced with two or more vinyl groups, and for example,

ethylene glycol diacrylate,
ethylene glycol dimethacrylate,
triethylene glycol dimethacrylate,
tetra ethylene glycol dimethacrylate,
1,3-butylene glycol dimethacrylate,
trimethylol propane triacrylate,
trimethylol propane trimethacrylate,
1,4-butane diol diacrylate,
neopentyl glycol diacrylate,
1, 6-hexanediol diacrylate,
penta erythritol diacrylate,
penta erythritol triacrylate,
penta erythritol tetraacrylate,
penta erythritol dimethacrylate,
penta erythritol trimethacrylate,
penta erythritol tetramethacrylate,
glycerol dimethacrylate,
glycerol diacrylate,
glycerol allyloxy dimethacrylate,
1,1,1-trishydroxymethyl ethanediacrylate,
1,1,1-trishydroxymethyl ethanetriacrylate,

1,1,1-trishydroxymethyl ethanedimetaacrylate,
 1,1,1-trishydroxymethyl ethanetri meta-acrylate,
 1,1,1-trishydroxymethyl propane diacrylate,
 1,1,1-trishydroxymethyl propane triacrylate,
 1,1,1-trishydroxymethyl propane dimethacrylate,
 1,1,1-trishydroxymethyl propane trimethacrylate,
 triallyl cyanurate,
 diallyl cyanurate,
 triallyl trimellitate,
 diallyl terephthalate,
 diallyl phthalate
 divinyl benzene etc. are mentioned.

Moreover, as the above "the cationic nature reactivity emulsifier which contains an allyl group in a molecule", the reactant emulsifier which contains quaternary ammonium salt shown by the following formula (S) is a typical thing.



(In the formula,

R₁ represents a hydrocarbon group with 8-22 carbon which may contain a substitution group,

R₂ and R₃ represent an alkyl group with 1-3 carbon,

R₄ represents a hydrogen atom or a methyl group,

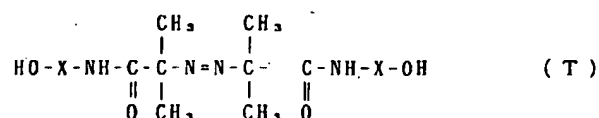
X represents the negative ion of monovalent.)

It is well known (Japan Unexamined Patent Publication Showa 60-78947), and is marketed as RATEMURU K-180 (a brand name, made by Kao Corp.).

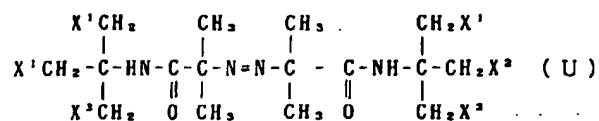
Here, the cationic nature reactivity emulsifier which is gradually taken into polymer during polymerization is suitable, as long as it is a cationic nature reactivity emulsifier which contains an allyl group that is a group with relatively low reactivity among those is widely included without limiting it to those mentioned above.

Moreover, it is good to for the amount of the cationic nature reactivity emulsifier containing an allyl group used to be in the range of 0.1-30 wt%, 0.5-5 wt%, to a gelled polymer particulate solid part 100 weight part.

As the polymerization start agent used in this case, the water soluble azoamide compound shown by the following general formula (T) or (U) are especially suitable.



(X represents a direct chain or a divergence alkylene group of 2-12 carbon in the formula)



(In the formula, at least one of X_1 , X_2 , and X_3 represents a hydroxyl group and the others represent hydrogen)

There are well known (Japan Unexamined Patent Publication Showa 61-218618, Japan Unexamined Patent Publication Showa 61-63643), and are marketed as VA series (a brand name, made by Wako Jun-yaku Industries Inc.).

The required quantity of the polymerization start agent is clear in the technical field concerned, and 0.1-1.5 weight part is optimal to the gelled polymer fine particle solid part 100 weight part.

When blending any of the above gelled polymer fine particles to the cationic electrodeposition paint composition (A) in this invention, it is desirable that the combination amount of this gelled polymer fine particle is 1-50 wt%, preferably 5-35 wt%, to the total resin solids containing the above-mentioned epoxy based cationic electrodeposition resin (a).

When the content of the gelled polymer fine particle in the cationic electrodeposition paint composition (A) is less than 1 wt% to the total resin solids, the control effect is small over the fall of coating film molten viscosity at the time of electrodeposition coating film baking, and the edge cover nature of electrodeposition coating film tends to become inadequate.

On the other hand, when it exceeds 50 wt%, it is not desirable since the leveling effect by heat flow of coating film of the electrodeposition paint composition (B) of the 2nd layer becomes inadequate and the flat and smooth nature of electrodeposition coating film becomes inferior.

In the case where the gelled polymer fine particle is used, as other granular compound, coloring pigments, such as titanium white, carbon black, (bengala / red ocher), yellow lead, etc.; constitution pigments, such as talc, calcium carbonate, mica, clay, silica, etc.; chromium pigments, such as strontium chromate, zinc chromate, etc.; lead pigments, such as basic silica lead, chromiomic lead, etc. may be used if necessary.

When using only pigments in the cationic electrodeposition paint composition (A) in this invention, it is desirable that the pigments with an oil absorption amount of 100 or more, preferably 150 or more, are contained by at least 5 wt%, preferably 10-95 wt%, more preferably 20-90 wt%, among all the pigments to be contained.

When blending the above-mentioned pigments, it is good to have the total oil absorption amount of all the pigments blended become in the range of 500-10,000, preferably 2,000-9,000, more preferably 3,000-7,000, to 100g of the epoxy based cationic electrodeposition resin (a).

The pigments with an oil absorption amount of 100 or more that can be used in this invention are, for example,
 anhydrous silicon dioxide,
 silicon dioxide system pigments, such as hydrous formless silicon dioxide,
 and carbon system pigments can be mentioned,
 and silicon dioxide system pigments is suitably used.

Since the above-mentioned carbon system pigments have conductivity in the pigments itself and they will reduce the painting workability of the cationic electrodeposition paint a little if they are used independently, it is desirable to use together and to blend with silicon dioxide system pigments.

The combined use rate of the silicon dioxide system pigments and carbon system pigments in this case can be set to the range of 9/1 – 6/4, preferably 8/2 – 7/3, by the weight ratio.

As the commercial article of the silicon dioxide system pigments with an oil absorption amount of 100 or more mentioned above, for example,

“EROJIRU 200”, a brand name by Japan EAROJIRU (oil absorption amount 143-183),

“SAIROIDO 244”, a brand name by Fuji Davison (oil absorption amount 270-330),

“SAIROIDO 404” (oil absorption amount 170-230),

“SAIROIDO 978” (oil absorption amount 180-230) etc. can be raised.

Moreover, as the carbon system pigments, the furnace type or channel type carbon black (oil absorption amount is usually 100-130) usually used as black pigments is used, and for example, the brand name “NEODUBEKUTORAMAAKU 11” made by the U.S. Colombian Carbon company, etc. can be mentioned.

In addition to the above-mentioned pigments with an oil absorption amount of 100 or more, the pigments usually used for the electrodeposition paints, for example,
 inorganic coloring pigments, such as (bengala / red ocher), titanium white, etc.;
 constitution pigments, such as talc, clay, calcium carbonate, etc.,
 can be used together as long as the total oil absorption amount of all the pigments to 100g of the resin ingredients in the electrodeposition paint is in the range of 1500-10,000.

The total oil absorption amount of these pigments is measured by the following method using JIS K 5101-78 (the pigments examination method).

The sample of the standard amount is correctly measured to 10mg to parchment paper, and this is

moved onto the board of frosted glass.

The quantity of the required boiling linseed oil is calculated beforehand from the oil absorption amount expected about the sample, about 90% of it is taken from micro PYURETTO to the tip of a steel spoon, and the sample on the frosted glass board and the boiling linseed oil are immediately kneaded together fully for about 5 minutes.

The operation in which 1-2 drops of the boiling linseed oil are added and kneaded are repeated subsequently, the time when the whole sample becomes one collected lump of uniform hard putty for the first time is set as the terminal point, and the quantity of the boiling linseed oil required by then is read to 0.01mL.

The oil absorption amount of each pigment is computed by the following formula from this.

$$A = L/S \times 100$$

A: Oil absorption amount

S: Mass of a sample (g)

L: Amount of the boiling linseed oil used (g)

Therefore, total oil absorption amount is computed by adding all the values multiplied the value of the oil absorption amount of each pigment computed by the above-mentioned formula with the combination amount of each pigment (g) to the resin 100g.

When the combination amount of the pigments with an oil absorption amount of 100 or more is less than 5 wt% of all pigments in the case where the pigments are used with the cationic electro-deposition paint composition (A) in this invention, it is not desirable since the electrodeposition paint of the 2nd layer stops being able to deposit easily, when the total oil absorption amount of the pigments is less than 1500, it is not desirable since the edge cover nature becomes inadequate, and when it exceeds 10,000, it is not desirable since the pigments become easy to condense and become the cause of abnormal coating surface (bumps, dry rough skin, etc.).

The cationic electrodeposition paint composition (A) obtained from the above-mentioned epoxy based cationic electrodeposition resin (a) and the above-mentioned particle-like ingredient (b) can thus be painted on the desired substrate surface by cationic electrodeposition painting.

Generally, cationic electrodeposition painting can be carried out by using electrodeposition bath which consists of the cationic type electrodeposition paint composition (A) that is diluted with deionized water etc. so that solid part concentration becomes about 5-40 wt% and is further adjusted in the range of pH 5.5-8.0.

The above-mentioned cationic electrodeposition paint composition (A) requires that the minimum molten viscosity at the time of hardening the obtained electrodeposition coating film should be in the range of 10^5 - 10^8 CPS from the point of edge cover nature.

This minimum molten viscosity means the minimum value when the viscosity of coating film first becomes lower than the initial value and then becomes high rapidly in the process which coating

film hardens by baking.

According to the rolling sphere system viscosity measuring method given in JIS-Z-0237, this minimum molten viscosity is determined from the heat flow appearance of the scratched scar by contrast with the paste with a known viscosity.

Next, the cationic electrodeposition paint composition (B) that is applied as the electrodeposition coating film for the above-mentioned un-cured cationic electrodeposition paint composition (A) according to this invention, has the cationic electrodeposition resin (c) whose surface tension is in the range of 25-45 dyne/cm, or preferably in 28-40 dyne/cm as its main component, and becomes the electrodeposition paint for the 2nd layer of the electrodeposition paint.

It is necessary for the cationic electrodeposition resin (c) to have a smaller surface tension than that of the epoxy based cationic electrodeposition resin (a) which becomes the 1st layer.

As it is explained above, there is no specific limit for the cationic electrodeposition paint composition (B) as long as the resin used have all the features listed above, and it can be consisted of the same composition as in the usual cationic electrodeposition paint composition.

As for the cationic electrodeposition resin (c) which fulfills the above-mentioned conditions and can be applied for the cationic electrodeposition paint composition (B), there are amine added epoxy resin acrylic resin, polyester resin, etc.

Among these, it is most desirable to use an addition reaction product of at least one of epoxy resin, an acrylic resin, and polyester resin and a basic amino compound, or acrylic resin to which a monomer having cationic group is copolymerized, and for example,

(I) a denatured epoxy polyamine resin in which a lactone group is introduced into the main chain or the side chain;

(II) an addition reaction product of an acrylic resin and an amino group containing compound to which a monomer component having an epoxy group (glycidyl group) is copolymerized; and

(III) an acrylic resin to which a monomer component having amino group is copolymerized, can be mentioned.

As for an example of the denatured epoxy polyamine resin of the above (I), the denatured epoxy polyamine resin which is obtained by adding polyphenol compounds, such as bisphenol A, and amino group containing compound to an addition reaction product which is obtained by adding ϵ -caprolactone to a secondary hydroxyl group in a hydroxyl group contained epoxy resin with 200-400 of epoxy amount in a presence of catalysts such as an organic tin compound etc., can be mentioned.

In this case, it is desirable for the quantity of the ϵ -caprolactone residue group in the above-mentioned resin is in the range of 5-40 wt%, or preferably in the range of 10-30 wt%.

This denatured epoxy poly amine resin can be used by being mixed with hardening agents, such as block isocyanate, or can be made to have self-cross-linking nature by making this denatured epoxy poly amine resin react with a partial block isocyanate.

As for the addition reaction product of an acrylic resin and an amino group containing compound used for the cationic electrodeposition resin (c), for example, an acrylics denatured polyamine resin which is obtained by adding amino group containing compound to a glycidyl group in the acrylic resin to which a polymerizable glycidyl compound like a glycidyl acrylate and a glycidyl meta-acrylate etc., is copolymerized, can be mentioned, and furthermore, the resin which is obtained by adding polyphenol compounds, such as bisphenol A, and an amino group containing compound to the above-mentioned glycidyl group containing acrylic resin can be mentioned.

Moreover, as for an example of the acrylic resin of (III), an amino group containing acrylic resin obtained by copolymerizing amino group containing (meta) acrylates, such as a dimethylaminoethyl meta acrylate and amino group containing (meta) acrylics amide, such as dimethylamino ethylmethacryl amide with the other unsaturated monomers if needed, can be mentioned.

These resins can be cured by using the above-mentioned isocyanate compound.

Moreover, it is also possible to use an acrylic resin and a non-ionic polyester resin with an excellent weather-proof characteristic along with the above-mentioned resin used for the cationic electrodeposition resin (c).

It is necessary for the cationic electrodeposition resin (c) used in this invention to have its surface tension of 25-45 dyne/cm or preferably 28-40 dyne/cm.

When the surface tension is smaller than 25 dyne/cm, the adhesion between the 1st and the 2nd layers of the coating film formed will not be sufficient enough, and the adhesion between the electrodeposition multiple layer coating film and the glazing coating film will also decrease.

On the other hand, when the surface tension exceeds 45 dyne/cm, since it becomes easy to be mixed with the 1st layer white coating film, it becomes hard to form a domain layer coating film.

It is necessary that the surface tensions of the epoxy based cationic electrodeposition resin (a) and the cationic electrodeposition resin (c) are in the above-mentioned ranges and the surface tension of the resin (a) is larger than that of the resin (c), and it is preferable to chose and combine the two resins so that the differences in between the surface tensions of the resin (a) and that of the resin (c) will be more than 5 dyne/cm or preferably be in the range of 10-20 dyne/cm.

Furthermore, when a cross-linking agent etc., is added to the resin (a) and the resin (c) in order to make them into a clear emulsion, the surface tension of the whole solid part in the clear emulsion of the resin (a) should be larger than that of the whole solid part in the clear emulsion of the resin (c).

It is also possible to add the usual paint additives, such as coloring pigments like carbon black, titanium white, and bengala / red ocher; constitution pigments like clay, talc, and calcium carbonate;

rust resistance paints, such as chromic strontium and chromic lead;
or other additive agents to the above-mentioned cationic electrodeposition paint composition (B).

As for the other additive agents, for example,
dispersion assistant agents (non-ionic surface-active agent);
repelling prevention agents for the surface to be coated (acrylic resin, fluoro resin, silicone resin,
etc.);
and hardening catalysts (salt of metal, such as a lead, bismuth and tin) etc., are mentioned.

The above-mentioned cationic electrodeposition paint composition (B) can be prepared into the composition whose solid part concentration is in the range of about 5 to about 40 wt%, and whose pH is about 5.5 to about 8 by being diluted with deionized water.

In this invention, as for the method and the equipment for carrying out the electrodeposition paint using the above-mentioned paint composition (A) and (B), the method and the equipment which has been used for the cationic electrodeposition paint can be applied here also.

Here, it is desirable to make the material to be coated as cathode and to make a carbon board as an anode

Although the electrodeposition paint condition used here is not especially limited, it is generally set at

Bath temperature: 15-35DEGC (preferably 20-30DEGC),

Voltage: 100-400V (preferably 200-300 V),

Current density: 0.01-3 A/dm²,

Electrification time: 30 second-10 minutes,

Area ratio (A/C) 6/1-1 / 6

Distance between poles: 10-100cm,

and by agitating;

in order to carry out electrodeposition of each paint composites.

The film thickness (dry state) of the electrodeposition coating film of the 1st layer formed by using the above-mentioned electrodeposition, should in the range of 5-30 μm , or preferable to be in the range of 10-25 μm , and the film thickness (dry state) of the electrodeposition coating film of the 2nd layer which is applied on the 1st layer should be in the range of 5-70 μm or preferable to be in the range of 10-50 μm .

In this invention, it is desirable to first ring the excess electrodeposition paint on the surface of the material to be coated by an immersing method or a spraying method using an extra filtrate, reverse osmosis membrane filtered solution, or deionized water, after the 1st electrodeposition paint, and then to carry out the 2nd electrodeposition paint.

Moreover, although it is necessary to carry out the 1st electrodeposition coating and the second electrodeposition paint when they are yet non-cured for the forming of a multiple layer coating and for the adhesiveness of the coatings, it is also possible to heat the 1st electrodeposition paint, for example, at the temperature less than 120 DEGC after being rinsed, or to heat it with hot air so that

the excess moisture is removed, and therefore, the “non-cured state” include the half-cured state also in this invention.

After being rinsed with deionized water or reverse osmosis membrane filtered solution preferably, the electrodeposition coating film with two layers formed on the surface of the material to be coated is heated at the temperature which is higher than the hardening starting temperature of the paint composition (B), preferably at the temperature range of 100-250DEGC, or more preferably at the temperature range of 120-200DEGC, and is cured.

The film thickness of the electrodeposition coating film which is the sum total of the film thicknesses of the 1st electrodeposition coating layer and 2nd electrodeposition coating layer should be in the range of 15-80 μm .

It is possible to finish the electrodeposition coating film formed in this way by repeatedly apply glazing paints if needed.

When the 1st and the 2nd electrodeposition paints are performed according to the method of this invention, the electrodeposition coating film applied in the 2nd coating is deposited on the surface of the electrodeposition coating film of the 1st coating, and the coating film with multiple layers of the 1st electrodeposition layer and the 2nd electrodeposition layer can be formed.

And by following the method of this invention, it is possible to cover the edge parts with the 1st layer of the electrodeposition paint film, and to maintain the surface smoothness and the uniform film characteristic with the 2nd layer of the electrodeposition paint film.

Consequently, the weak points that the prior electrodeposition coating film had, such as the rust resistance of the edge parts of the materials to be coated, can be remarkably improved and a thick film is formed even which is excellent in its surface smoothness can be formed, and it is possible to be used as a corrosive protection painting method for the industrial paint field, such as a car, electric apparatus, and a prefab steel frame.

(Execution example)

Hereafter, although this invention is explained in more detail with execution examples, this invention is not limited to these.

In the execution and comparison examples, “part” indicates “weight part” and “%” indicates “weight%”.

Manufacture examples of a cationic nature epoxy resin

Synthetic example 1

Under the nitrogen gas blowing, 525 part of propylene oxide denatured bisphenol A glycidyl ether (note 1) and 36 part of methyl isobutyl ketone solution (80% of active ingredients) of ketimine of monoethanol amine and methyl isobutyl ketone were prepared in a reaction container with a

thermometer, an agitating equipment, a reflux cooler, and a nitrogen gas blowing opening, and they were heated at 160 DEGC until an epoxy group was disappeared.

Furthermore, 665 part of bisphenol A glycidyl ether with the amount of epoxy of about 190 and 232 part of methyl isobuthyl ketone solution of ketimine of mono ethanol amine and methyl isobuthyl ketone with 80% of active ingredients were added to this, and it was made to react at 140DEGC until the epoxy group concentration became 0.27mmol./g.

The epoxy resin solution with the number average molecular weight of about 1500 was obtained.

Next, it was diluted and cooled with 365 part of ethylene glycol monobuthyl ether, and 100 part of solution (80% of active ingredients) of methyl isobuthyl ketone of diethylene toriamine and methyl isobuthyl ketone of diketimine was added when the temperature became 100 DEGC, and it was again made to react at 100 DEGC until the increase in viscosity was no more seen, and finally an epoxy poly amine resin solution with 81% of solid parts was obtained.

The surface tension of this resin was 53 dyne/cm.

Synthetic example 2

Under the nitrogen gas blowing, 518 parts of epoxy resin with its number average molecular weight of 370 and the amount of epoxy of 185 obtained by the reaction of bisphenol A and eroxypropyl diethylenetriamino, 57 parts of bisphenol A and 0.2 parts of dimethyl benzilamine were prepared in a reaction container with a thermometer, an agitating equipment, a reflux cooler, and a nitrogen gas blowing opening, and they were heated at 120 DEGC until the amount of the epoxy group became to be 250.

Subsequently, 213 parts of ϵ -caprolactone 213 part and 0.03 parts of tetra butoxy titanium were added and were heated up to 170 DEGC, and samples were taken out while maintaining the temperature in order to investigate the amount of non-reacted ϵ -caprolactone by an infrared absorption-spectrum measurement, and when the reaction ratio became to be more than 98%, 148 parts of bisphenol A and 0.4 parts of dimethyl benzilamine were added to it, and it was made to react at 130 DEGC until the amount of the epoxy became to be 936.

Next, after adding 257.4 part of methyl isobuthyl ketone, 25.6 part of diethylamine, and 68.3 part of diethanol amine, and making it react at 80 DEGC for 2 hours, it was dilutes with 143.4 part of methyl ethyl ketone, and resin solution with 72% of solid parts was obtained.

The surface tension of this resin was 40 dyne/cm.

Manufacture of cationic electrodepositon paint clear emulsion

Creation example 1

By mixing 92.6 parts of the cationic nature epoxy resin (solid part 75 parts) obtained in the synthetic example 1 and 27.8 parts of blocked diisocyanate (solid part 25 parts), adding 1.8 parts of

90% acetic acid to it, and by adding 190.3 parts of deionized water while mixing, neutralizing, and agitating the mixture with a high-speed agitating machine, clear emulsion (1) with 32% of solid part was obtained.

Creation example 2

By carrying out the same process as the creation example 1 except for replacing 92.6 parts of the cationic nature epoxy resin obtained in the synthetic example 1 with 104.2 parts of the cationic nature epoxy resin obtained in the synthetic example 2 and for changing the amount of deionized water to 178.7 parts, clear emulsion (2) with 32% of solid part was obtained.

Creation example 3

By mixing 48.6 parts of the cationic nature epoxy resin (solid part 35) obtained in the synthetic example 2, 28.9 parts of blocked diisocyanate (solid part 26) and 54.8 parts of non-ionic acrylic resin (solid part 39), adding 1.8 parts of 90% acetic acid to it, and by adding 178.4 parts of deionized water while mixing, neutralizing, and agitating the mixture with a high-speed agitating machine, clear emulsion (3) with 32% of solid part was obtained.

Manufacture of an acrylics copolymer (for gelled polymer fine-particles)

Reference example 1

After adding 320 parts of isopropyl alcohol to a 1L capacity flask equipped with an agitating equipment, a thermometer, a cooling pipe, and a heating mantle, it was heated up to the reflux temperature (about 83 DEGC) while being agitated.

The mixture of the following monomer and the polymerization start agents were dropped into this over 2 hours at the reflux temperature (about 83-87DEGC).

Styrene	272 parts
n-buthyl acrylate	224 parts
2-hydroxyethylacrylate	80 parts
dimethylaminoethyl metaacrylate	144 parts
KBM-503*	80 parts
azobis isobutyronitrile	24 parts

* γ -methacrylxy propyltri methoxysilane (Product of Shin-Etsu Chemical Inc.)

Subsequently, after being agitated for 30 more minutes, a solution in which 8 parts of azobisdimethyl valeronitrile was dissolved in 120 parts of isopropyl alcohol was dropped into to it over 1 hour, and after being agitated again for about 1-hour, 320 parts of isopropyl alcohol was added, and it was cooled.

An acrylics copolymer varnish with 51% of solid parts, 64 of amine value, 48 of hydroxylic base value, and 20, 000 of the number average molecular weight was obtained.

Reference example 2

By using the blow listed monomer mixture and by following the same process as in the reference example 1, an acrylics copolymer varnish was obtained.

isobuthyl acrylate	480 parts
2-hydroxyethylacrylate	80 parts
dimethylaminoethyl meta acrylate	160 parts
KBM-503	80 parts

The obtained acrylics copolymer varnishes had 50% of solid parts, 71 of amine value, 43 of hydroxylic base value, and 15, 000 of the number average molecular weight.

Manufacture of a gelled polymer fine particle

Manufacture example 1

After adding 780 parts of the acrylics copolymer varnish obtained in the reference example 1 and 6.4 parts of acetic acid into a 2L capacity flask and agitating it at 30 DEGC for 5 minutes, 1156 parts of deionized water was dropped into to it over 30 minutes while being agitated roughly, and it was again agitated for 3 hours after being heated up to 70-80 DEGC.

A milky color internally cross-linked gelled polymer fine-particle dispersion solution with 20% of solid part was obtained in this way, and the average diameter of particles in ethylene glycol monobuthylether was 0.15 μm (it was measured with NANOSAIZA-N-4 produced by Coulter Inc.)

Manufacture example 2

By carrying out the same process as in the manufacture example 1 except for replacing the acrylics copolymer varnish obtained in the reference example 1 with the one obtained in the reference example 2, an internally cross-linked gelled polymer fine-particle dispersion solution was obtained.

The average diameter of particles in ethylene glycol monobuthyl ether was 0.20 μm .

Manufacture example 3

After adding 480 parts of acrylics copolymer varnish obtained in the reference example 1 into 2L capacity flask, 196 parts of cationic acidity colloidal silica water dispersion solution "ADERAITO CT-300" (Product of Asahi Denka Kogyo K.K.) and 4.0 parts of acetic acid was added to it while being agitated, and after it was agitated for 5 hours at about 30 DEGC, 740 parts of deionized water was dropped into to it over 30 minutes while being agitated roughly, and it was again agitated for 3 hours after being heated up to 70-80 DEGC.

A milky color internally cross-linked gelled polymer fine-particle dispersion solution with 20% of solid parts was obtained in this way.

And therefore, the gelled polymer fine particle dispersion solution was obtained.

The average diameter of the particles of this particle in water was 0.08 μm .

Manufacture example 4

After adding 3507.5 parts of deionized water and 80 parts of RATEMURU K-180 (Product of Kao Corp., 25% solution) to a 1L capacity flask equipped with an agitating equipment, a thermometer, a cooling pipe, and a heating mantle, it was heated up to the reflux temperature while being agitated.

20% of the bathing solution mixture in which 12.5 parts of VA-086 (Product of Wako Jun-Yaku Industries Inc.) which was a polymerization start agent was dissolved in 500 parts of deionized water was added to this.

5% of the following monomer mixture was added after 15 minutes was passed.

Styrene	430 parts
n-buthyl acrylate	440 parts
1.6-hexanediol diacrylate	40 parts
2-hydroxyethylacrylate	40 parts
KBM-503*	50 parts

* γ -methacrylxy propyltori methoxysilane (Product of Shin-Etsu Chemical Inc.)

Subsequently, after agitating it for 30 more minutes, remaining monomer mixtures and polymerization start agent solution were dropped.

The monomer mixture was added over 3 hours and the polymerization start agent solution was added over 3 to 5 hours while keeping the polymerization temperature at 90 DEGC.

After heating it for 30 minutes while keeping the temperature at 90 DGEC even after the dropping of polymerization start agent solution was ended, it was cooled to the room temperature, and it was filtered and was taken out using a filter cloth.

The gelled polymer fine particle with 20% of solid parts and 0.07 μm of average diameter of the particles was obtained in this way.

Adjustment of the cationic electrodepositon paint composition (A) and (B)

Preparation example 1

75 parts of gelled polymer fine particle dispersion solution with 20% of solid parts obtained in the

manufacture example of 1 and 61.1 parts of pigment past (1) with 43% of solid parts were added to 313 parts of the clear emulsion (1) with 32% of solid parts obtained in the creation example 1 while being agitated, and after it was diluted with 258 parts of deionized water, the cationic electrodeposition paint (A-1) with 20% of solid parts was obtained.

Preparation example 2

Polyamide denatured epoxy resin and blocked diisocyanate whose surface tensions were 53 dyne/cm was added to 286 parts of the clear emulsion for the cationic electrodeposition with 35% of solid parts which is used as a vehicle component, along with the gelled polymer fine particle dispersion obtained in the manufacture example of 2 and pigment past (1) in the same amount used in the manufacture example 1 while being agitated, and after it was diluted with 258 parts of deionized water, the cationic electrodeposition paint (A-2) with 20% of solid parts was obtained.

Preparation example 3

By carrying out the same process as in the preparation example 1 except for replacing the gelled polymer fine particle dispersion solution obtained in the manufacture example 1 with the gelled polymer fine particle dispersion solution obtained in the manufacture example 3, the cationic electrodeposition paint (A-3) with 20% of solid parts was obtained.

Preparation example 4

By carrying out the same process as in the preparation example 2 except for replacing the gelled polymer fine particle dispersion solution obtained in the manufacture example 2 with the gelled polymer fine particle dispersion solution obtained in the manufacture example 4, the cationic electrodeposition paint (A-4) with 20% of solid parts was obtained.

Preparation example 5

134 parts of the above-mentioned pigment paste (2) with 43% of solid parts were added to 313 parts of clear emulsion with 32% of solid parts (1) obtained in the creation example 1, and after it was diluted with 342 parts of deionized water, the cationic electrodeposition paint (A-5) with 20% of solid parts was obtained.

Preparation example 6 (for comparison)

By carrying out the same process as in the preparation example 1 except for replacing clear emulsion (1) with clear emulsion (2) with 32% of solid parts obtained in the creation example 4, the cationic electrodeposition paint (A-6) with 20% of solid parts was obtained.

Preparation example 7 (for comparison)

131.95 parts of the above-mentioned pigment paste (3) with 43% of solid parts were added to 313 parts of clear emulsion with 32% of solid parts (1) obtained in the creation example 1, and after it

was diluted with 339.5 parts of deionized water, the cationic electrodeposition paint (A-7) with 20% of solid parts was obtained.

Preparation example 8

61.1 parts of the above-mentioned pigment paste (1) with 43% of solid parts were added to 313 parts of clear emulsion with 32% of solid parts (2) obtained in the creation example 1, and after it was diluted with 257.8 parts of deionized water, the cationic electrodeposition paint (B-1) with 20% of solid parts was obtained.

Preparation example 9

By carrying out the same process as in the preparation example 8 except for replacing clear emulsion (2) with clear emulsion (3) with 32% of solid parts obtained in the creation example 3, the cationic electrodeposition paint (B-2) with 20% of solid parts was obtained.

Preparation example 10 (for comparison)

61.1 parts of the above-mentioned pigment paste (1) with 43% of solid parts were added to 313 parts of clear emulsion with 32% of solid parts (1) obtained in the creation example 1, and after it was diluted with 257.8 parts of deionized water, the cationic electrodeposition paint (B-3) with 20% of solid parts was obtained.

Execution examples and Comparison examples

A electrodeposition painting board with the 1st layer which has its film thickness of 10 μm (based on dryness film thickness) and the 2nd layer which has its film thickness of 20 μm was obtained by carrying out the electrodeposition painting according to the process listed in Table 2 using the cationic electrodeposition paint obtained in the above-mentioned preparation examples in the combination listed in Table 3.

Similarly, the paint results and the coating film performance are collectively shown in Table 3.

Each examination in Table 3 was performed according to the following method.

[Performance test method]

(*1) The surface tension of the electrodeposition resin and the electrodeposition coating film molten viscosity at the time of baking were measured as mentioned above.

The numerical value of the surface tension is indicated with dyne/cm and the numerical value of the molten viscosity is the minimum viscosity and indicated with cps.

(*2) Cross section covering nature: The material to be coated was set in a salt spraying equipment so that the edge parts is placed vertically, and the corrosive protection nature of the edge part after 168 hours was measured by carrying out the salt-water spraying examination of J1SZ2371.

□: no rust generation

O: Rust was generated slightly.

X: Rust was generated remarkably.

(*3) Flatness and smoothness of the surface to be coated: It was measured by looking at the finish of the electrodeposition painting with naked eyes.

O: good

▲: almost good.

□: little poor

(*4) Warm water secondary immersing adhesion: After immersing the material in water at 40 DEGC for 20 days, grid marks are made on the surface of the material according to JIS K 5400-19796.15, and after pasting a cellophane tape on to the surface, and the surface was evaluated after taking the tape off rapidly.

□: No damage and good

O: The edge of the grid is exfoliated slightly.

▲: A grid of squares are exfoliated.

(*5) Warm water-proof spraying: After cross cutting the electrodeposition coating film with a knife which reaches to the foundation and carrying out the salt water spraying examination for 1000 hours according to JISZ2371, rust from the cut part and swelling width were measured.

(*6) 2 coated weather-proof: After coating it with aminoalkyd resin system paint aramic clear (Product of Kansai Paint CO., Ltd.) on top of the baked electrodeposition board, it is baked for 15 minutes at 140 DEGC.

This board is applied to a sunshine weatherometer for 20 hours, and was given a cross cut per 1 cycle (one cycle: immersing the board in water at 40 DEGC for 20 hours), and the exfoliation examination was carried out with cellophane adhesion tapes.

The numbers of cycles taken to generate exfoliation was measured by repeating this examination.

Applicant (140)

Kansai Paint CO., Ltd.

72. Inventor

Masafumi Kume

72. Inventor

Yasuyuki Hirata

Table 1

	Pigment Paste		
	(1)	(2)	(3)
60% quaternary ammonium salt containing epoxy resin	5.73	5.73	5.73
Titanium oxide (Oil absorption amount 22)	13		39
Refined Cray (Oil absorption amount 43)	7.03	15.9	11
Carbon black* (Oil absorption amount 40)	0.5	3.2	1
Graphite (Oil absorption amount 40)		5.3	
SAIROID 22 ** (Oil absorption amount 300)		27.5	
CF BOUSEI C-100LB*** (Oil absorption amount 30)	2.3		2.3
Deionized water	32.53	76.39	72.92
Total	61.09	134.02	131.95
Pigment absorption amount	677	8765	1440

*.Asahi carbon Corp. Brand name "Carbon ASM"

**SAIROIDO 244 ... Product of Fuji Davison, Brand name, Water formless silicon dioxide paints

***CF POUSEI C-100LB ...Product of Kikuchi Coloring Industry, Brand name, basic silica lead

Table 2

Painting process		Painting condition
1. Foundation		Cold rolling dull steel sheet: 0.8X300X90mm (the angle of the side and the surface is at 45 degree)
2. Surface treatment		PAARUBONNDO #3030 treatment (Nihon PAKARAISINGU Inc., zinc phosphate system)
3. Electodeposition coating (1)	Electodeposition	Voltage: 300V Bath temperature: 30 DEGC pH: 6.5
	Rinsing	Dionized water is sprayed.
4. Electodeposition coating (2)	Electodeposition	Voltage: 300V Bath temperature: 30 DEGC pH: 6.5
	Rinsing	Dionized water is sprayed.
5. Baking		180 DEGC x 30 minutes

Table 3

			Execution example						Comparison example		
			1	2	3	4	5	6	7	8	9
Paint	1st layer	Electodeposition coating (A)	A-1	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-1
		Surface tension of electodeposition resin *1	53	53	53	53	53	53	40	53	53
		Molten viscosity *1	10 ⁷	10 ⁷	10 ⁶	10 ⁷	10 ⁷	10 ⁷	10 ⁷	10 ²	10 ⁷
	2 nd layer	Electodeposition coating (B)	B-1	B-2	B-2	B-1	B-1	B-1	B-2	B-1	B-3
		Surface tension of electodeposition resin	40	40	40	40	40	40	40	40	53
Characteristic of the coating film	Edge cover *2		□	□	O	□	□	□	O	X	O
	Surface flatness*3		O	O	O	O	O	O	O	O	□
	Warm water secondary immersing adhesion *4		□	□	□	□	□	□	O	O	O
	Warm water-proof spraying *5		2.0	2.0	2.0	2.0	2.0	2.0	3.0	2.5	2.0
	2 coated weather-proof *6		2	4	4	2	2	2	4	2	1